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Crystallization of $BaO \cdot TiO_2$-SiO_2-Al_2O_3 Glasses and Dielectric Properties of their Crystallized Products

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In order to prepare barium titanate ceramics having high dielectric constant by crystallization of glass, a series of glasses with the general composition $(100\text{-}x\text{-}y)BaO \cdot TiO_2 + xSiO_2 + yAl_2O_3$, in which x and y are within the range of 15 to 60 and 0 to 20 mole %, respectively, was investigated, especially with behavior during reheating and dielectric properties of their crystallized products.

I. INTRODUCTION

$BaTiO_3$ ceramics, which are widely employed as components of electronic devices, are usually prepared by sintering crystalline powders. Herczog[1] prepared $BaTiO_3$ ceramics by crystallization of glass which consists of melting the raw materials, forming the melts and crystallizing the formed glasses by heat treatment: Herczog investigated the crystallization of a series of glasses with the compositions $x BaTiO_3 + (100\text{-}x) BaAl_2Si_2O_8$ (x by weight) and obtained, from a glass of this system with addition of a small amount of fluoride, a glass-ceramics with a dielectric constant of 1200. The present author has found, however, that the glass used by Herczog has a high melting temperature and, in addition, is likely to devitrify during cooling of the melt. Such behavior is undesirable for production of the crystallized glass (glass-ceramics) with constant dielectric properties.

The present study has started from a search for compositions of glasses that are easy to be melted and also formed without devitrification. Glass formation tendency and crystallization behavior during reheating have been investigated for the compositions $(100\text{-}x\text{-}y)BaO \cdot TiO_2 + xSiO_2 + yAl_2O_3$, where x and y are varied in the range 15 to 60 and 0 to 20 in mole %, respectively. Also dielectric properties of the crystallized products have been measured and discussed on the basis of their chemical composition and microstructure.

II. EXPERIMENTAL PROCEDURE

II. 1. Preparation of Glasses

To determine the glass formation region in the system $BaO \cdot TiO_2$-SiO_2-Al_2O_3, glasses with the compositions $(100\text{-}x\text{-}y)BaO \cdot TiO_2 + xSiO_2 + yAl_2O_3$, where x and y were varied in the range of 15 to 60 and 0 to 20 mole %, respectively, were melted. As

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Table 1. Glass Composition

Specimen No.	Composition (mole %)		
	$BaO \cdot TiO_2$	SiO_2	Al_2O_3
1	60	20	20
2	60	26	14
3	60	30	10
4	60	34	6
5	63	27	10
6	54	36	10
7	45	45	10

batch materials were used reagent-grade barium carbonate, titanium oxide and aluminum hydroxide, and high-grade quartz powder of low iron content usually employed in the manufacture of optical glasses. About 50 g of the batch mixtures were put in a platinum crucible of 80 cc in capacity and melted at 1450°C for 1 hour in an electric furnace. The melts were poured on a steel plate, pressed into the form of plates approximately 2 mm thick, and immediately annealed at 650°C in another furnace. Some of the glasses thus obtained, whose compositions are given in Table 1, were subjected to the following experiments.

II. 2. Differential Thermal Analysis

Crystallization behavior of glass was examined by the differential thermal analysis. A solid cylindrical piece of glass just fit to the DTA sample holder (6 mm in diameter and 14 mm in height) was used as sample to minimize the effect of surface crystallization, which might be serious with powder sample. A heating rate of 10°C/min was adopted and α-Al_2O_3 was used as reference material.

II. 3. Crystallization of Glasses

Glass slabs of the size $10 \times 10 \times 1.5$ mm cut from the plate and ground with No. 2000 Al_2O_3 powder were crystallized by heating on a platinum sheet in an electric furnace. They were heated up at a rate of 5°C/min from room temperature to 1100°C, kept there for 1 hour and cooled in the furnace. The resultant crystallized samples were subjected to the visual observation of the appearance, x-ray diffraction analysis and measurements of dielectric properties.

II. 4. X-ray Diffraction Analysis

Identification of crystals precipitating in the course of crystallization and determination of the amount of $BaTiO_3$ crystals found in the final crystallized products were conducted by the x-ray diffraction analysis with powdered samples. To determine the $BaTiO_3$ crystal content, intensity of the (101) reflection of $BaTiO_3$ crystals in the sample was measured with the use of the (220) reflection of fluorite (CaF_2) as an internal standard and compared with a calibration curve. The calibration curve was obtained with intimate mixtures of known amounts of $BaTiO_3$ crystals, glass of the composition No. 2 and fluorite crystal. Volume fraction V of the $BaTiO_3$ crystals was calculated from the measured density D_m of the crystallized sample by the formula

$V=x(D_m/D)$, where x is the weight fraction determined by the x-ray analysis and $D=6.06$ g/cm^3 is the density of $BaTiO_3$.[2)]

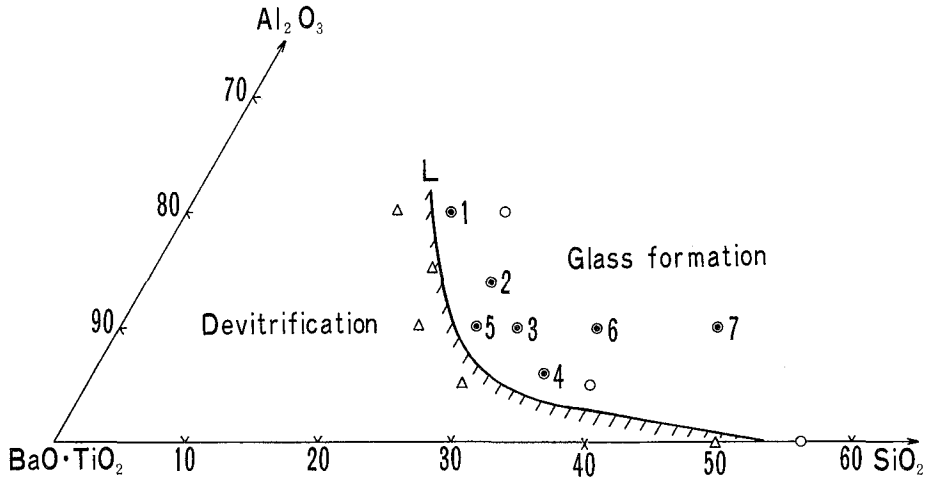
II. 5. Measurement of Dielectric Properties

Dielectric properties were measured at a frequency of 1Mc/s at room temperature. The measurements were made by a Q-Meter (Type GM-102, Yokogawa Electric Works, Ltd.). Since some of the crystallized glasses showed non-uniform surface, all the samples were ground to rectangular pieces of the size $10\times10\times1$ mm to remove the effect of original surfaces. Silver paste applied on both faces of the samples served as electrodes.

III. RESULTS

III. 1. Glass Formation Region

Glass formation region in the system $BaO\cdot TiO_2$-SiO_2-Al_2O_3 is shown in Fig. 1. The sign (○) or (◉) in Fig. 1 refer to the composition which gave a transparent glass when the melt heated at 1450°C was poured onto a steel plate. Especially the sign (◉) refers to the glass composition which was used for further investigation. The numbers given correspond to those of the compositions given in Table 1. The sign (△) refers to the composition which did not give an entirely transparent glass due to the formation of scums at melting temperature or partial devitrification during cooling. The sign (×) refers to the composition whose melt was completely devitrified during cooling. A solid line L gives a tentative boundary representing a limit of glass formation.



○, ◉ No devitrification (◉Composition used for making crystallized specimens).
△ Partial devitrification or scum.
× Extreme devitrification.

Fig. 1. Glass formation area in the system $BaO\cdot TiO_2$-SiO_2-Al_2O_3.

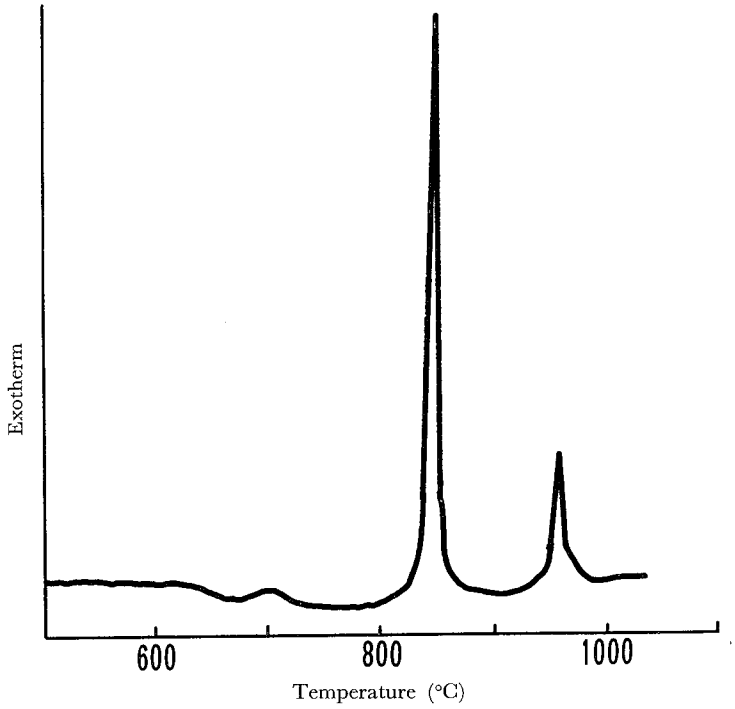


Fig. 2. Differential thermal analysis of the glass; $BaO \cdot TiO_2$ 60, SiO_2 26, Al_2O_3 14 mole % (Specimen No. 2).

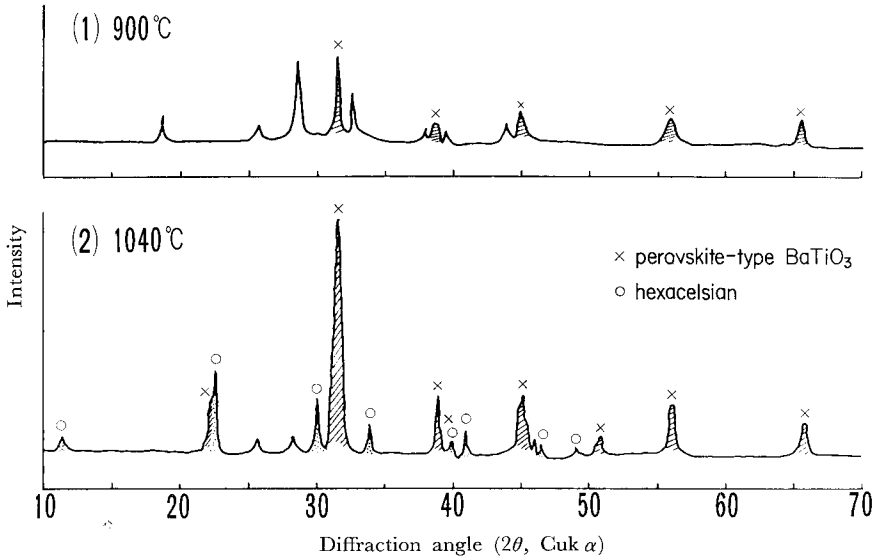


Fig. 3. X-ray diffraction patterns of the crystallized glasses of 900° and 1040°C. Composition of the parent glass: $BaO \cdot TiO_2$ 60, SiO_2 26, Al_2O_3 14 mole %.

III. 2. Differential Thermal Analysis and X-Ray Diffraction Analysis

A thermogram of the glass No. 2 ($BaO \cdot TiO_2$ 60, SiO_2 26, Al_2O_3 14 mole %) is given in Fig. 2. Two exothermal peaks are observed, one at 850°C and the other at 960°C. Powder x-ray diffraction patterns of the samples heated to the temperatures 900°C and 1040°C which are a little over each peak temperature are shown in Fig. 3. It is seen from Fig. 3(1) that in the sample heated at 900°C a considerable amount of perovskite-type $BaTiO_3$ crystals are precipitated as indicated by the strong lines designated by (×). In addition, there is an unidentified crystalline species to which the lines at $2\theta = 18.7°$, 25.9°, 28.6°, 32.7°, 37.9°, 39.5° and 43.9° are attributed. In the sample heated at 1040°C (Fig. 3 (2)), there are a great amount of $BaTiO_3$ crystals and a less amount of the unidentified crystal, as evidenced from the growth and weakening of the corresponding diffraction lines. Further, a series of new diffraction lines designated by the sign (○) in the figure appears. These lines can be attributed to the hexacelsian ($BaAl_2Si_2O_8$). Herczog[1] also found that the $BaTiO_3$ crystals are precipitated at lower temperatures and then hexacelsian crystals are precipitated at higher temperatures in the course of crystallization of the glass having the composition $BaTiO_3$ 74 and $BaAl_2Si_2O_8$ 26% by weight (BaO 42.4, TiO_2 34.8, SiO_2 15.1 and Al_2O_3 7.7 mole %). No description was made, however, of the unidentified crystal by Herczog.

The kind of crystals and the amount of $BaTiO_3$ crystal found in the samples

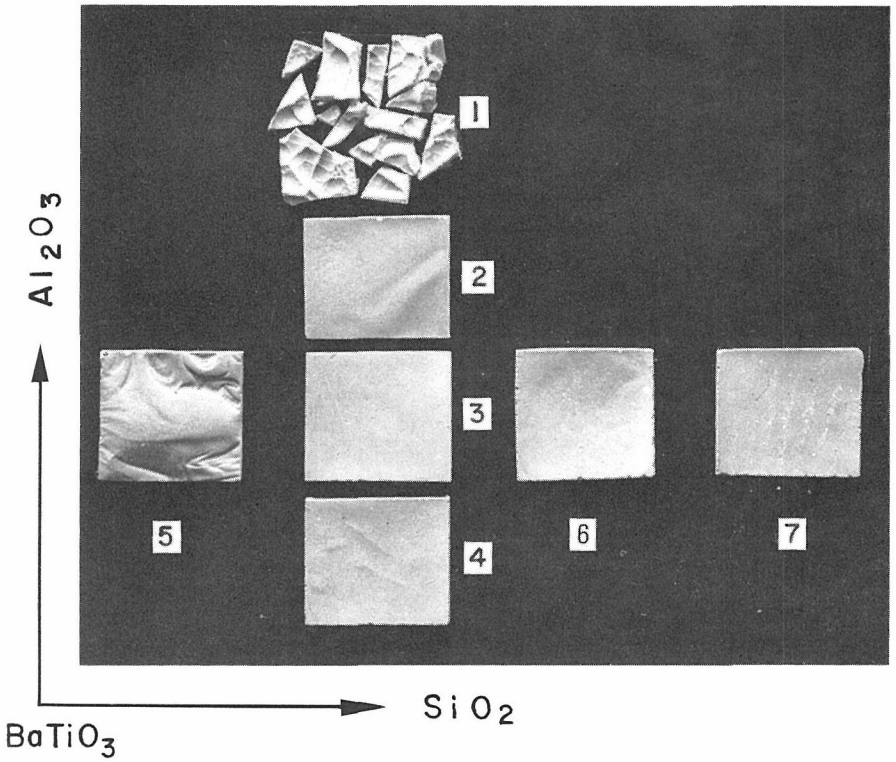


Fig. 4. Appearance of crystallized products obtained by heating up to 1100°C.

Table 2. Crystalline Phases and Dielectric Properties.

Specimen No.	1	2	3	4	5	6	7
Crystalline phases*	BT	BT	BT	BT	BT	BT	—
	BAS	BAS	BAS	BAS	BAS	BAS	BAS
	—	—	BTS	BTS	—	BTS	BTS
	X	X	X	X	X	X	X
Content of $BaTiO_3$ (vol %)	19	23	15	8	18	7	0
Dielectric properties							
Parent glass							
ε	18	17	17	16	17	17	14
$\tan\delta$	0.0021	0.0023	0.0020	0.0023	0.0020	0.0022	0.0019
Crystallized product							
ε	168	500	284	77	415	76	23
$\tan\delta$	0.0174	0.0250	0.0207	0.0119	0.0304	0.0173	0.0020

* BT; $BaTiO_3$ (perovskite-type), BAS; Hexacelsian ($BaAl_2Si_2O_8$), BTS; $BaTiSiO_5$ X; Unidentified crystal.

crystallized by heating to 1100°C by a schedule described in paragraph **II. 3.** are given in Table 2. It can be seen from Table 2 that crystals precipitated in the crystallized glasses are perovskite-type $BaTiO_3$, hexacelsian, $BaTiSiO_5$ and unidentified crystals.

III. 3. Defects of Crystallized Glasses

The appearances of the crystallized glasses obtained by heating to 1100°C are shown in Fig. 4. Although most of the crystallized glasses show no defect, the crystallized sample of the composition No. 1 has a great number of cracks and that of the composition No. 5 has surface ripple. In general, the compositions containing too much amount of Al_2O_3 or $BaO \cdot TiO_2$ tend to give the crystallized glasses having defects such as cracks or surface ripples.

III. 4. Dielectric Properties

III. 4-1. Effects of Heat Treatment

Figure 5 shows the dielectric properties (dielectric constant and $\tan\delta$) of the glass No. 2 as a function of temperature of heat treatment. All the measurements were made at room temperature. The glass was heated up at a rate of 5°C/min from room temperature to a temperature (temperature of heat treatment mentioned above) and then taken out immediately from the furnace. It can be seen from the figure that the dielectric constant of the glass first remains almost the same at about 17 up to 700°C and then increases as the temperature of heat treatment is raised. The rate of increase is particularly great in the temperature range from 800°C toward 1100°C, where the value reaches 560. The heating up to still higher temperatures affects the dielectric constant only slightly.

Dielectric properties of the same glass kept at 1100°C for various periods are shown in Fig. 6. The glass was heated at a rate of 5°C/min from room temperature to 1100°C. The figure shows that both dielectric constant and $\tan\delta$ do not vary with heating time. In other words, at 1100°C dielectric properties characteristic of the maximum heating

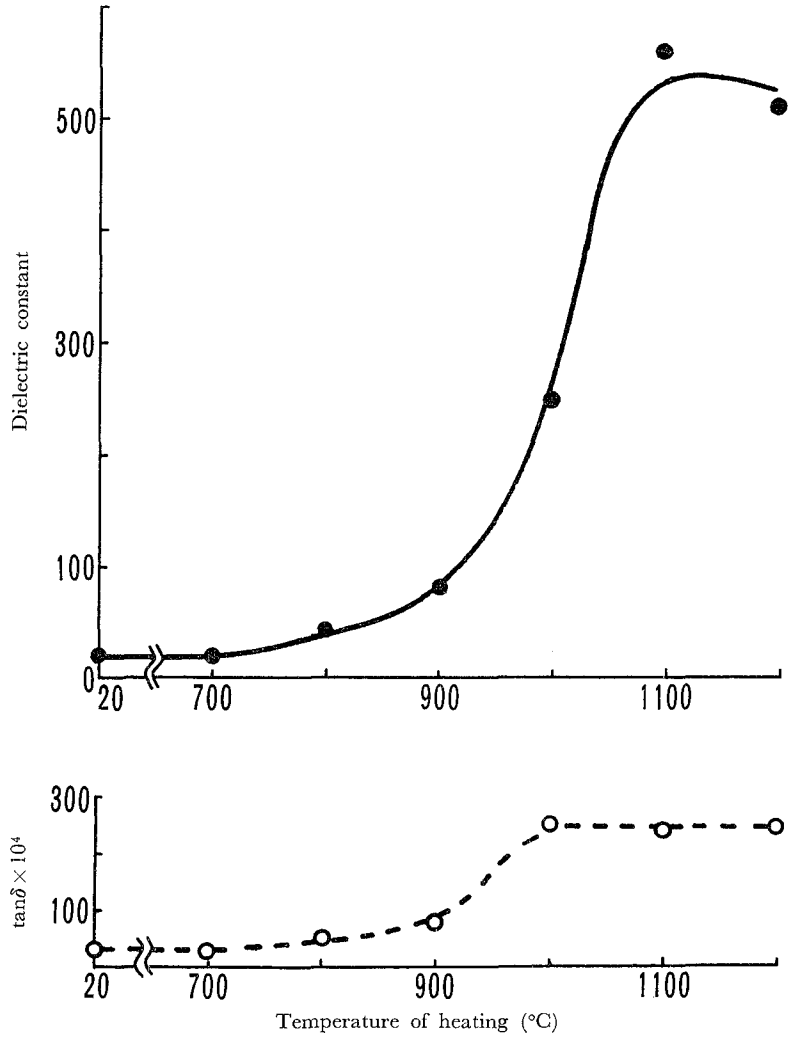


Fig. 5. Dependence of dielectric properties upon heating temperature for the glass; $BaO \cdot TiO_2$ 60, SiO_2 26, Al_2O_3 14 mole %.

temperature (1100°C) are attained as soon as the temperature is reaches.

III. 4-2. Effects of Chemical Composition

The values of dielectric constant and tanδ of the crystallized glasses obtained by heating to 1100°C are shown in Table 2. The data on the glasses before heat treatment are also shown in the table. The dielectric constants of the crystallized glasses are reproduced in a composition triangle in Fig. 7. In this figure the values shown by paretheses represent the amounts (volume fraction) of $BaTiO_3$ crystal precipitated in the crystallized samples. It is seen from Table 2 that the dielectric constant of the parent glass shows only slight dependence on the chemical composition, varying within the range from 14 to 18, whereas that of the crystallized glass is very much dependent on the chemical composition of the parent glass, varying from 23 to 500. Figure 7

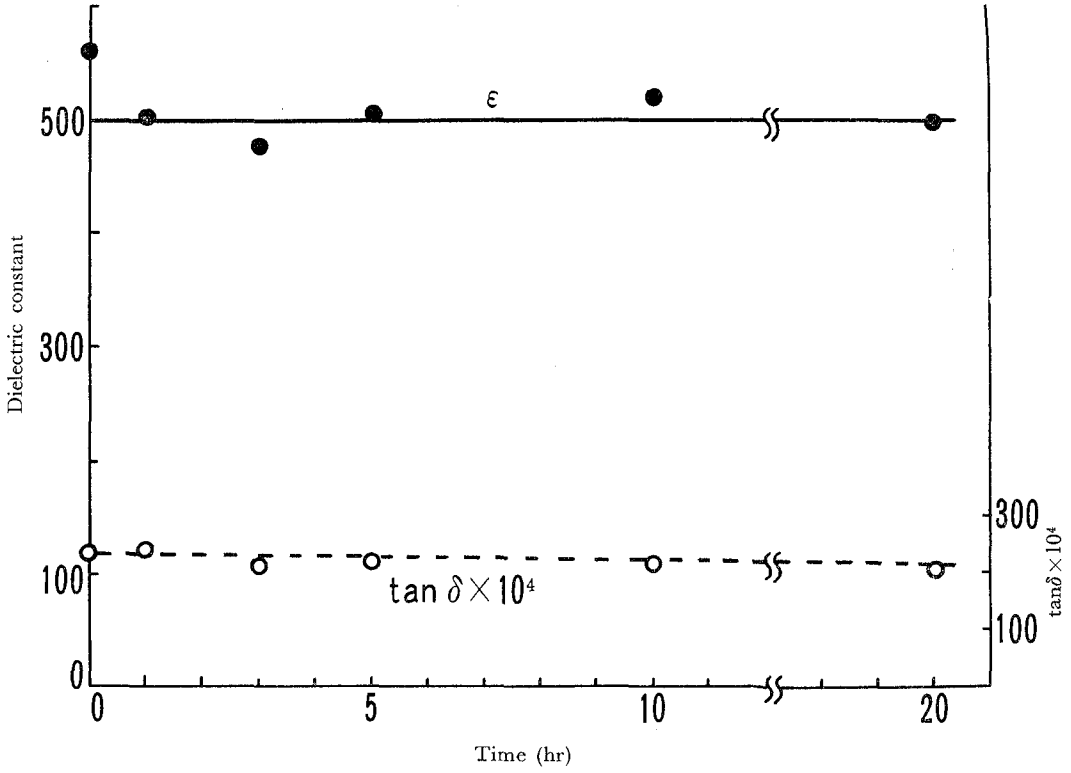
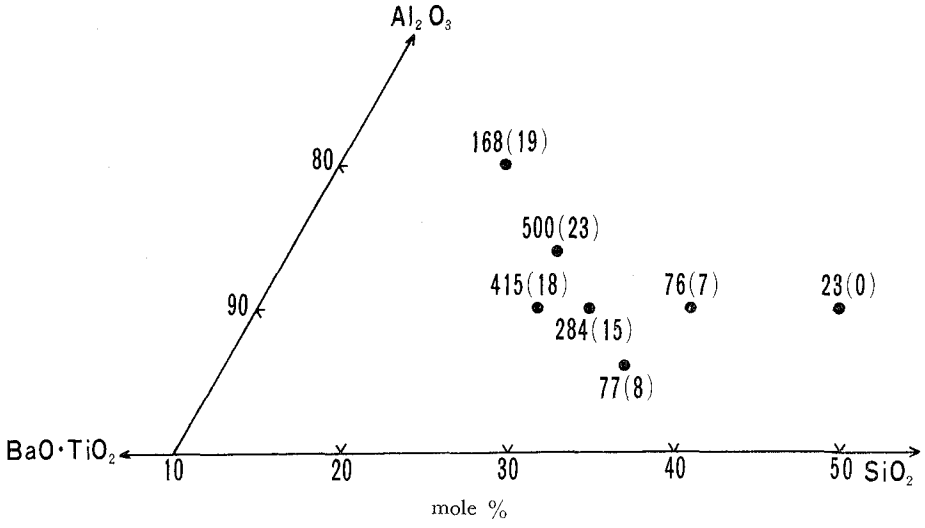


Fig. 6. Dependence of dielectric properties upon heating time.
Heating temperature: 1100°C.
Composition of glass: $BaO \cdot TiO_2$ 60, SiO_2 26, Al_2O_3 14 mole %.



a (b) a: Dielectric constant
b: Content of $BaTiO_3$ (vol. %)

Fig. 7. Dielectric constant and content of barium titanate of the crystallized products.

shows that with constant Al_2O_3 content the dielectric constant of the crystallized glass decreases as the $SiO_2/BaO{\cdot}TiO_2$ mole ratio increases and with constant $BaO{\cdot}TiO_2$ content the dielectric constant reaches a maximum when the Al_2O_3/SiO_2 mole ratio is 35/65.

IV. DISCUSSION

IV. 1. Dependence of Dielectric Constant on Chemical Composition

It was shown in the foregoing section that the dielectric constant of the crystallized glass is very much dependent on the chemical composition of the parent glass. This may be attributed to the dependence of the amount of $BaTiO_3$ crystal precipitated in the crystallized glass on the chemical composition. The comparison of the dielectric constant with $BaTiO_3$ crystal content (Fig. 7) confirms that, in general, the dielectric constant increases with increasing volume fraction of $BaTiO_3$ crystal. The crystallized glass of the composition No. 1 (dielectric constant 168 and crystal content 19 in Fig. 7) exhibits a considerably low dielectric constant, however, in spite of relatively high content of $BaTiO_3$ crystal present: The reason for this rather exceptional case may be explained in terms of cracks present in the crystallized glass.

IV. 2. Microstructure of Crystallized Glass

The crystallized glasses in the present system are regarded as the mixture of a high dielectric constant phase consisting of $BaTiO_3$ crystals and a low dielectric constant phase consisting of residual glass and other crystals than $BaTiO_3$. In general, the dielectric constant of the mixture depends on the dielectric constant, volume fraction, shape and arrangement (regular or irregular) of the constituent phases and the type of mixing. Mixtures are devided into two classes by the type of mixing, one is "pure mixture" consisting of only particles and the other is "porphyritic mixture" in which particles are dispersed in another continuous phase.

Bruggeman[3] has derived relationships between the dielectric constant of the mixture (ε) and the volume fractions (δ_1 and δ_2) of the constituent phases for the following four cases.

(A) Three dimensional pure mixture of lamellar particles irregularly dispersed:

$$\varepsilon = 1/2(-\varepsilon_\perp + \sqrt{\varepsilon_\perp(8\varepsilon_{/\!/} + \varepsilon_\perp)})$$

(B) Three dimensional pure mixture of spherical particles irregularly dispersed:

$$\varepsilon = 1/4(2\varepsilon_{/\!/} - \varepsilon_{/\!/}' + \sqrt{(2\varepsilon_{/\!/} - \varepsilon_{/\!/}')^2 + 8\varepsilon_1\varepsilon_2})$$

(C) Three dimensional porphyritic mixture in which lamellar particles are irregularly dispersed in matrix:

$$\varepsilon = \varepsilon_1(3\varepsilon_2 + 2\delta_1(\varepsilon_1 - \varepsilon_2))/(3\varepsilon_1 - \delta_1(\varepsilon_1 - \varepsilon_2))$$

(D) Three dimensional porphyritic mixture in which spherical particles are irregularly dispersed in matrix:

$$1 - \delta_1 = (\varepsilon_1 - \varepsilon)(\varepsilon_2/\varepsilon)^{1/3}/(\varepsilon_1 - \varepsilon_2)$$

Here

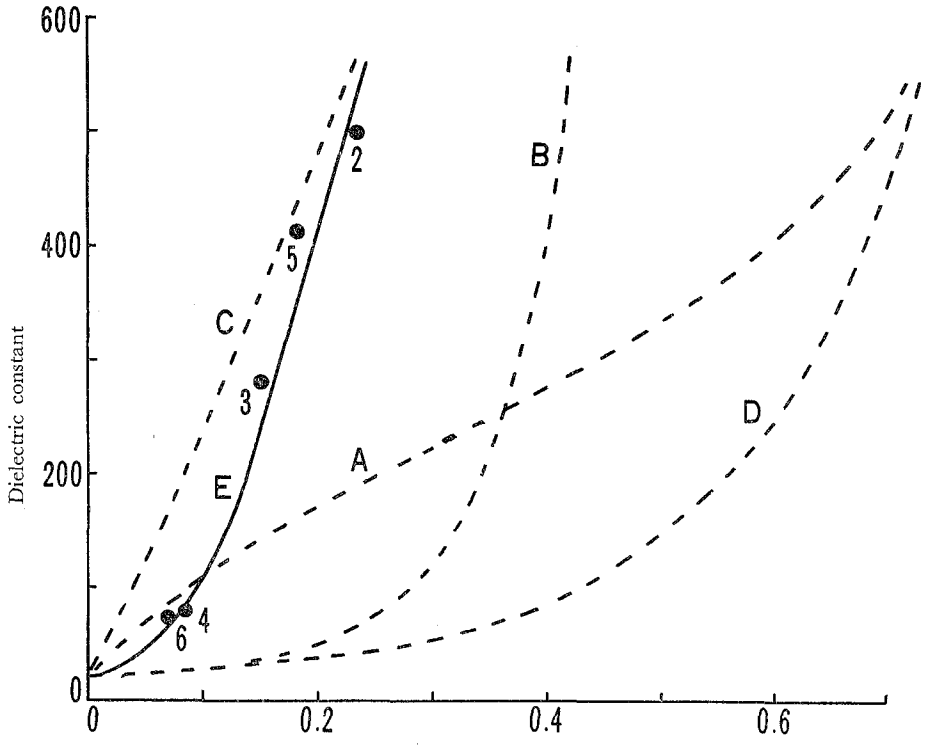
$1/\varepsilon_{\perp} = \delta_1/\varepsilon_1 + \delta_2/\varepsilon_2$,

$\varepsilon_{/\!/} = \delta_1\varepsilon_1 + \delta_2\varepsilon_2$,

$\varepsilon_{/\!/}' = \delta_1\varepsilon_2 + \delta_2\varepsilon_1$, and

ε_1 and ε_2 = dielectric constant of each constituent phase.

Figure 8 shows the dependences of dielectric constant of the mixture on volume fraction of $BaTiO_3$ calculated for the above four cases. In the calculation the dielectric constant of $BaTiO_3$ crystals was assumed 3300, a value which was obtained by extrapolating the measured dielectric constants of the crystallized glasses to the $BaTiO_3$ volume fraction of unity. The dielectric constant of the other phase was assumed 20, a value which is nearly equal to the dielectric constants of the parent glasses and their crystallized products containing no $BaTiO_3$ crystal. The solid circles in Fig. 8 represent the experimental data obtained on the crystallized glasses of the composition given in Table 1. The solid line was drawn so that it might fit best to the experimental data. It can be seen from the figure that the equation (C) describes the experimental results



A: Pure mixture of lamellar particles.
B: Pure mixture of spherical particles.
C: Porphyritic mixture in which lamellar barium titanate crystals are dispersed in matrix.
D: Porphyritic mixture in which spherical barium titanate crystals are dispersed in matrix. (A—D: Calculated from Bruggemans equations)
E: The experimental results by the author.

Fig. 8. Dielectric constant as a function of $BaTiO_3$ content.

best. Therefore the crystallized glasses in this system are assumed to have the structure of porphyritic mixture in which lamellar barium titanate crystals with dielectric constant of 3300 are irregularly dispersed in matrix consisting of residual glass and crystal phases such as $BaAl_2Si_2O_8$ and $BaTiSiO_5$ with dielectric constant of 20. Deviation of experimental data from Bruggeman's relationship (C) at the region of low $BaTiO_3$ content may be attributed to the different size or shape of the $BaTiO_3$ crystals at low $BaTiO_3$ content from at high $BaTiO_3$ content. More detailed studies, however, are required for elucidating this matter.

Herczog[1] also investigated the relation between the dielectric constant of the crystallized glass and the volume fraction of constituent $BaTiO_3$ crystal for the glasses with the composition $x BaTiO_3 + (100-x) BaAl_2Si_2O_8$ (x by weight) and reported that experimental data fit best to the relationship (B) for pure mixture of spherical particles, in contrast to the present results obeying the relationship (C). The reason for this is not known. Further study is required.

V. SUMMARY

1. Glass formation region in the system $BaO \cdot TiO_2$-SiO_2-Al_2O_3 was determined and it was confirmed that the glasses containing higher amounts of BaO and TiO_2 components can be prepared in the present system containing Al_2O_3 than in the system $BaO \cdot TiO_2$-SiO_2.

2. Crystallization of the glasses in this system started at about 850°C and was essentially completed at about 1100°C. Crystals precipitated in the glasses heated to 1100°C were perovskite-type $BaTiO_3$, hexacelsian ($BaAl_2Si_2O_8$), $BaTiSiO_5$ and some unidentified crystals. Crystallized products obtained from the present glasses containing too much amount of $BaO \cdot TiO_2$ or Al_2O_3 showed defects such as cracks and surface ripples.

3. Dielectric properties of the crystallized products varied with the composition of the parent glass. With constant Al_2O_3 content, the dielectric constant decreased with increasing $SiO_2/BaO \cdot TiO_2$ mole ratio. With constant $BaO \cdot TiO_2$ content, it reached a maximum when the Al_2O_3/SiO_2 mole ratio was 35/65. Generally, the dielectric constant increased with increasing amount of $BaTiO_3$ crystals precipitated in the crystallized products. The highest dielectric constant measured in the present experiments was 500 at a frequency of 10^6c/s, that was obtained with the crystallized glass of the composition $BaO \cdot TiO_2$ 60, SiO_2 26, Al_2O_3 14 mole %.

4. The dielectric constant-$BaTiO_3$ volume fraction relationship of the crystallized glass agreed best with a Bruggeman's theoretical formula obtained by assuming that the crystallized glass has the structure of porphyritic mixture in which lamellar $BaTiO_3$ crystals are dispersed in matrix of residual glass and other crystals.

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